GeCp2big [Cp-big = C-5(CH2C6H4-iPr)(5)]

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Published in:
Zeitschrift fur Anorganische und Allgemeine Chemie

DOI:
10.1002/zaac.201200242

Publication date:
2013

DOI: 10.1002/zaac.201200242

$GeCp^{big}_2$ [Cp^{big} = $C_5(CH_2C_6H_4$-*i*Pr$)_5$]: A Flexible Sandwich Molecule

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Dedicated to Professor Hartmut Bärnighausen on the Occasion of His 80th Birthday

Keywords: Equilibrium; Germylene; Cyclopentadienyl ligands; Quantum chemical calculations; Sandwich molecules

Abstract. $GeCp^{big}_2$ (**1**) [Cp^{big} = $C_5(CH_2C_6H_4$-*i*Pr$)_5$] was synthesized by a reaction of KCp^{big} either with a GeCl solution or $GeCl_2$ and was obtained as colorless crystals. The molecular structure of **1** was determined by X-ray diffraction, showing that **1** features two penta-hapto bonded Cp^{big} ligands in a bent configuration with a Cp^{big}-Ge–Cp^{big} angle of 161°. Two out of ten benzyl substituents point towards the lone pair at the germanium atom so that two molecules fit perfectly together, leading to a dimeric arrangement of **1** within the solid state. Two polymorphs of **1** could be isolated, where **1** is oriented in a different way. As indicated by quantum chemical calculations, the open structure, where all benzyl substituents point away from the germanium atom is only disfavored by 21.6 kJ·mol^{-1}. In the open structure a bent arrangement is still realized, giving access to the lone pair at the germanium atom for further applications, e.g. in coordination chemistry.

Introduction

Metalloid cluster compounds of germanium of the general formula Ge_nR_m [$n > m$; R = ligand like $Si(SiMe_3)_3$ or $N(SiMe_3)_2$] are ideal model compounds for molecular entities in the grey area between molecules and the solid state. They give direct insight into the processes taking place on formation or dissolution of elemental germanium at the atomic scale.[1] As the dimensions of these metalloid clusters are in the nanometer range, the synthesis of metalloid clusters also opens the possibility to get first structural information on nano-particles, an important prerequisite for structure-property relations in this area.

In the last couple of years we were able to show that the disproportionation reaction of group 14 monohalide solutions constitutes a fruitful route to metalloid group 14 cluster compounds.[2] This route allows the formation of metalloid clusters at low temperatures, hence metastable intermediates can be trapped by kinetic stabilization.[3] The need to perform the reactions of the obtained monohalide emulsions directly in the co-condensation apparatus is thereby a significant drawback of this method.[4]

However, applying P*n*Bu_3 as a donor component during the co-condensation reaction leads to an isolable germanium(I) halide solution, which can be used outside the co-condensation apparatus in normal Schlenk glass-vessels and which can be stored at –78 °C for several weeks without decomposition. Thus, now a greater variety of ligands and a better control of the reaction conditions is available for the synthesis of metalloid germanium clusters applying the disproportionation of a germanium(I) halide.[5] In the following we present initial results using the potassium salt of the large cyclopentadienyl ligand Cp^{big} [Cp^{big} = $C_5(CH_2C_6H_4$-*i*Pr$)_5$].

Results and Discussion

A $Ge^{I}Cl$ solution is synthesized via co-condensation of the high temperature molecule $Ge^{I}Cl$ with a 10:1 mixture of toluene/P*n*Bu_3. The orange-red metastable solution can be stored at –78 °C over several weeks without decomposition. Reacting this solution with 1.1 equivalents of K[$C_5(CH_2C_6H_4$-*i*Pr$)_5$] leads to a dark brown reaction solution, which is stable at room temperature. On work-up of the reaction solution a yellow pentane extract is obtained from which colorless crystals of $GeCp^{big}_2$ (**1**) [Cp^{big} = $C_5(CH_2C_6H_4$-*i*Pr$)_5$] are obtained in 21 % yield and whose molecular structure is shown in Figure 1. Compound **1** results thereby from the oxidation product $GeCl_2$ of the disproportionation reaction: $2GeCl \rightarrow GeCl_2 + Ge$

As no elemental germanium is obtained during the reaction, germanium rich clusters and nanoparticles are still in solution, which is obvious from the dark brown color of the toluene extract. However, up until now we did not succeed in isolating one of the metalloid clusters of composition $Ge_n(Cp^{big})_m$ ($n > m$) and herein the structure of **1** is discussed.

$GeCp^{big}_2$ (**1**) is another ferrocene-like sandwich molecule of the heavier group 14 elements (Si, Ge, Sn, and Pb), which represent the most extensive series of isolated main group

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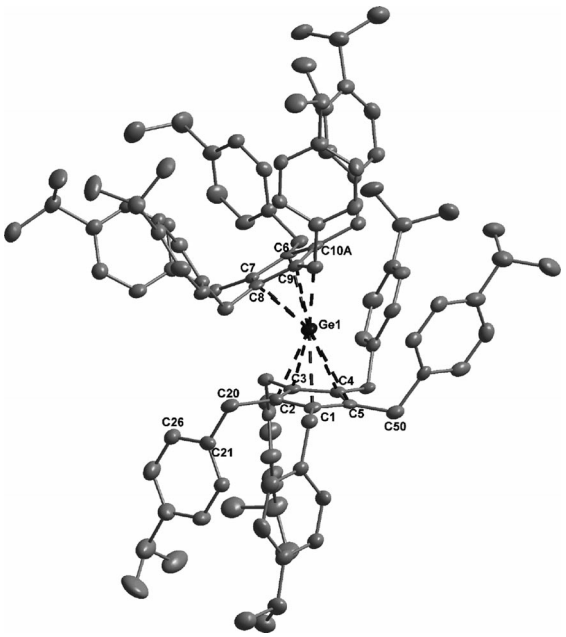


Figure 1. Molecular structure of $GeCp^{big}_2$ (**1**) [Cp^{big} = $C_5(CH_2C_6H_4$-*i*Pr)$_5$] , hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths /pm and angles /°: Ge–Cp(C1–C5): 224.2(2); Ge–Cp(C6–C10A): 220.7(3), Ge1–C1: 254.5(3), Ge1–C2: 244.5(4), Ge1–C3: 245.8(3), Ge1–C4: 260.8(3), Ge1–C5: 266.8(4), Ge1–C6: 252.1(3), Ge1–C7: 241.2(3), Ge1–C8: 243.6(3), Ge1–C9: 257.6(2), Ge1–C10a: 263.8(4), C2–C20: 149.9(5), C5–C50: 151.8(5), C20–C21: 151.6(5), C21–C26: 138.8(5), Cp–Ge–Cp: 160.9(2) C1–C5–C50: 126.7(3), C2–C1–C5: 108.4(3), C7–Ge1–C3: 106.9(1).

metallocenes.[6] Most of these metallocenes exhibit a bent structure which can be attributed to a stereochemically active lone pair at the central atom (Figure 2).[7] This explanation has been widely adopted in interpreting the structures of group 14 metallocenes. Furthermore, numerous theoretical calculations have been performed, showing that the bent structure is energetically favored, supporting the experimental results.[8]

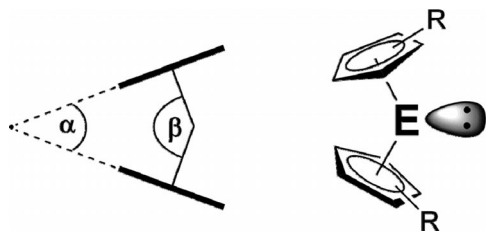


Figure 2. Model of the bent structure of a group 14 metallocene with the Cp–Ge–Cp angle *β*.

However, the stereochemical influence of the metal-centered lone pair is relatively low, and thus it is not surprising that metallocenes with a parallel configuration are known for all the heavier elements of group 14: Si,[9] Ge,[8e] Sn[10] and Pb.[11]

As can be seen from the molecular structure (Figure 1) **1** also exhibits a bent structure with a Cp–Ge–Cp angle *β* of 160.9°. The Ge–C distances vary from 243.6 pm to 266.8 pm showing that a distorted η^5 interaction is present. This is in line with the situation found in $Ge(Cp^{benz.})_2$ (**2**)[12] or $GeCp^*_2$ (**3**),[13] where the Ge–C distances are in the ranges 244.3–272.3 pm and 241.4–264.6 pm, respectively [$Cp^{benz.}$ = $C_5(CH_2C_6H_5)_5$, Cp* = C_5Me_5]. The most interesting feature of **1**, however, is that only eight of the ten *i*Pr-benzyl substituents point away from the germanium atom leading to a basket of five substituents on one side. On the other side two benzyl substituents are oriented towards the germanium atom, pointing directly to the lone pair. Therefore, this orientation is comparable to the one found for the pentabenzyl-Cp compound **2**, where no *para i*Pr substituent is present at the benzyl ring and where three of the ten benzyl substituents are oriented towards the lone pair.[12] Thus, the higher steric demand of *para*-*i*Pr-benzyl with respect to benzyl leads to a different arrangement, though the Cp–Ge–Cp angle β (Figure 2) is only slightly influenced being 160.9° in the case of **1** and 162.6° in the case of **2**.

Due to the fact that two benzyl substituents of one Cp^{big} ligand point towards the germanium atom, two different sites are present, which perfectly fit together as shown in Figure 3. Hence two of the benzyl substituents (4 and 5 in Figure 3) of one molecule fit within the area build up of three benzyl ligands (1, 2, and 3 in Figure 3) of the other molecule. This dimeric arrangement seems only due to crystal packing forces as no relevant C–H–π interactions[14] are present, i.e. all distances between hydrogen atoms and the centroid of aromatic rings of different molecules are longer than 3 Å.

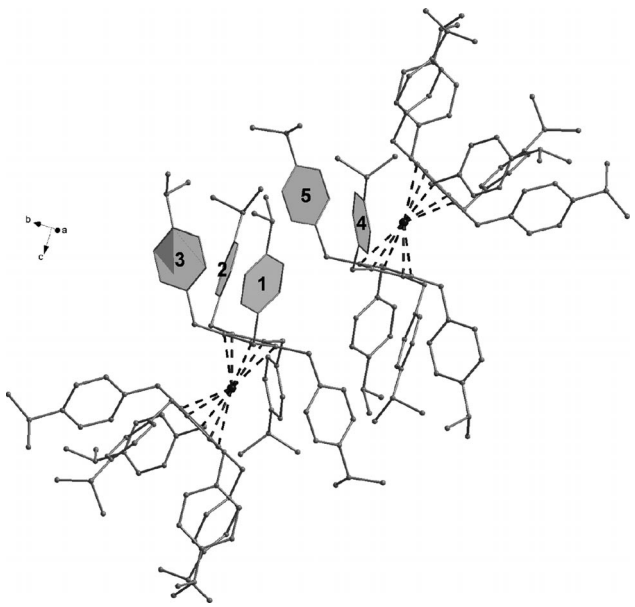


Figure 3. Dimeric unit of **1** within the solid state. The benzene rings of the benzyl substituents are emphasized by a polyhedral presentation.

However, these "dimers" can arrange differently in the solid state, depending on the amount of co-crystallized solvent molecules, as we were able to crystallize a second polymorph (**II**)[15] of **1** that also contains "dimers", which are now arranged in a different way.[16] In this second polymorph **II**, germylene **1** is arranged in a way, that the pentabenzyl baskets now form a closed area in which a pentane molecule is trapped and of

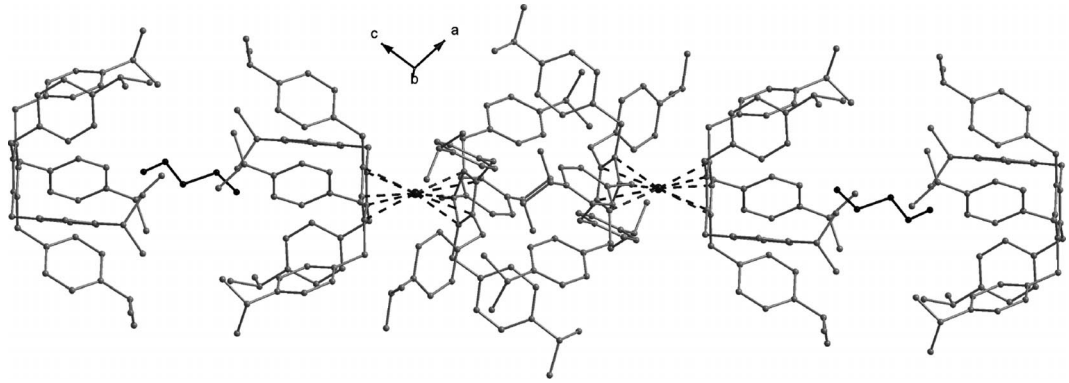


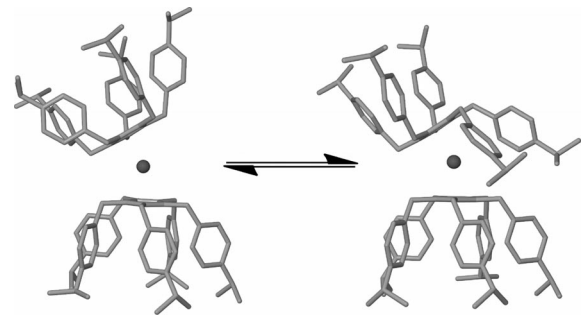
Figure 4. Arrangement of **1** within polymorph **II**; hydrogen atoms are omitted for clarity and the pentane molecules encapsulated by the 10 benzyl groups are shown.

which the atomic positions could be refined during crystal structure solution (Figure 4).

In the case of polymorph **I**, compound **1** is arranged less tightly, so that the pentabenzyl baskets do not point at each other. The co-crystallizing pentane molecules in polymorph **I** are arranged within the sheets of the "dimers" of **1**, which leads to a less effective crystal packing than the one in polymorph **II**, resulting in a slightly higher density for polymorph **II**.[17] Additionally, the volume of the asymmetric unit is ca. 4.2 % smaller in polymorph **II**, further indicating that a more dense packing is realized.

Nevertheless, the formation of "dimers" of **1** is the central structural feature of both polymorphs, which is only possible due to the fact that two benzyl rings of the Cp^{big} ligand of **1** point in the direction of the germylene lone pair. This arrangement seems unfavorable on first glance and might be the result of crystal packing forces. To further elucidate this aspect we performed quantum chemical calculations[18] on the gas phase structure of **1**, which show that the arrangement with two benzyl groups pointing to the germanium atom is indeed the structure with the lowest energy. However, the structure, where all ten benzyl substituents point away from the germanium atom, leading to two pentabenzyl baskets is energetically disfavored by only 21.6 kJ·mol^{-1}.[19] Thus, one might expect an equilibrium between the two forms in solution (Scheme 1). This assumption is corroborated by ^{1}H NMR measurements, in which we obtained just one set of signals for the benzyl substituents, showing that a fast equilibrium between the open and closed form (Scheme 1) is present in solution, averaging out the signals. Tests to freeze out the equilibrium failed, as only a slight broadening of the signals is observed at lower temperatures but no coalescence could be detected down to a temperature of –80 °C.

Taking a closer look at the calculated structure of the open form of **1** (Scheme 1), shows that the η^5 bound Cp^{big} ligands still exhibit a bent arrangement with a Cp^{big}–Ge–Cp^{big} angle $\beta = 159.7°$. This result indicates that the rotation of the benzyl substituent has a small influence on the bonding interaction between the germanium atom and the Cp^{big} ligand. However, the accessibility of the lone pair at the germanium atom differs significantly between the open and the closed form of the sandwich molecule **1**. While it might be readily accessible in the open structure, it is partially blocked in the closed form. Additionally, an electronic interaction is present. This can be seen by a comparison of the HOMO-2; being the best representation of the lone-pair (Figure 5); i.e. in the case of the closed form an interaction with one of the benzyl rings tilted to the germanium atom is realized. Although at first sight such lone-pair···π interactions seem unusual, they have been discussed for classical lone-pairs (O, N, F, Cl etc.) and electron-poor aromatic systems.[20]



Scheme 1. Equilibrium of the open and closed form of **1** in solution. The calculated molecular structures are shown (hydrogen atoms are omitted for clarity).

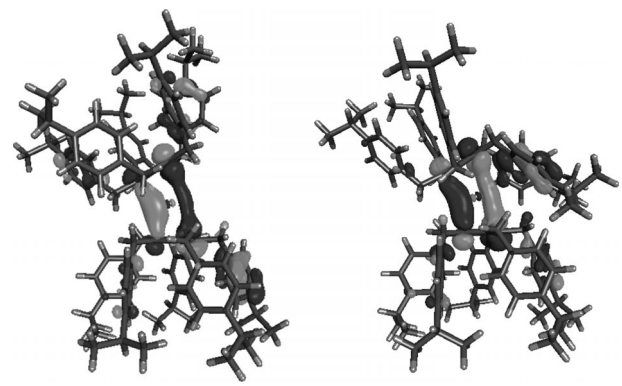


Figure 5. Representation of the HOMO-2 of the open (left) and closed (right) form.

Hence **1** might be an interesting compound for further tests on the accessibility of the lone pair in such highly crowded sandwich molecules of group 14 in e.g. coordination chemistry with transition metal compounds like Cr(CO)$_5$, or in subsequent reactions with small molecules like CO$_2$, CS$_2$, H$_2$, P$_4$, or S$_8$.[21] However, as the presented synthetic route via the disproportionation reaction is not useful for the synthesis of larger amounts of **1** we successfully checked if **1** is also accessible via a more classical synthetic route applying a stable precursor where germanium already exhibits the oxidation state +2. Thus, **1** can easily be synthesized in 92 % yield by the more convenient reaction of KCp^{big} with GeCl$_2$, so that further applications of this interesting flexible compound are possible.

Summary and Outlook

The reaction of a Ge^{I}Cl solution in toluene/P*n*Bu$_3$ with KCp^{big} [Cp^{big} = C$_5$(CH$_2$C$_6$H$_4$-*i*Pr)$_5$] gives the germylene GeCp$^{big}_2$ (**1**), which can be seen as the oxidation product of the disproportionation reaction of Ge^{I}Cl. Compound **1** is also obtained in 92 % yield by the more convenient reaction of KCp^{big} with GeCl$_2$ and appears in different polymorphic forms (**I** and **II**). Within the solid state, two of the ten CH$_2$–C$_6$H$_4$–*i*Pr groups point towards the germanium atom, being the minimum structure according to quantum chemical calculations. However, the open form, where all ten benzyl substituents point away from the germanium atom and where a bent arrangement is still realized is disfavored by only 21.6 kJ·mol^{-1}. It is therefore likely that a dynamic system is present in solution, which is corroborated by the fact that in solution only one set of signals is observed for the CH$_2$–C$_6$H$_4$–*i*Pr groups in the ^{1}H NMR spectroscopy. Consequently, the heavy carbene **1** can expose its shielded electron-pair on demand and could have interesting reactivities in coordination chemistry or towards small molecules like CO$_2$, CS$_2$, H$_2$, P$_4$, or S$_8$.[21] Apart from stoichiometric reactivity, investigation of its catalytic capability could be rewarding. In this respect, recent applications of germylenes in the controlled living radical polymerization of styrene, methacrylates, and urethanes should be mentioned.[22] Additionally, future research will concentrate on the isolation and structural characterization of the deeply colored reduction products of the disproportionation reaction, i.e. the metalloid clusters, to get further insight in the interesting reaction system Ge^{I}Cl and KCp^{big}.

Experimental Section

Synthesis of GeCp$^{big}_2$ (1): (a) A metastable Ge^{I}Cl solution was synthesized applying a co-condensation technique, where germanium (3.578 g, 49.3 mmol) reacted with HCl (40 mmol) at 1600 °C and where the resulting Ge^{I}Cl was condensed at –196 °C with a mixture of toluene and P*n*Bu$_3$ in a volume ratio of 10:1. After warming up to –78 °C, an orange-red solution was obtained. 20 mL of this solution (2.0 mmol GeCl) were transferred into a –78 °C cold flask, where KCp^{big} (1.68 g, 2.2 mmol) was present. The reaction mixture was slowly warmed to room temperature and a dark red nearly black reaction solution was obtained. The solvent was removed in vacuo and the brown residue was extracted with pentane (5 mL) leading to a yellow pentane extract. Storing this pentane solution at –28 °C for one day led to colorless crystals of Ge[C$_5$(CH$_2$C$_6$H$_4$-*i*Pr)$_5$]$_2$·pentane (yield 704 mg, 0.46 mmol, 21 %).

(b) GeCl$_2$·dioxane (17 mg, 0.07 mmol) were dissolved in benzene (0.5 mL) and KCp^{big} (80 mg, 0.14 mmol) was added. The reaction mixture was stored at 60 °C for one day leading to a yellow solution of Ge[C$_5$(CH$_2$C$_6$H$_4$-*i*Pr)]$_2$. The solvent was removed and 85 mg (0.06 mmol, 92 %) of the product were obtained as a pale yellow solid.

^{1}H NMR (C$_6$D$_5$CD$_3$): δ = 1.15 [d, 30 H, CH(C*H*$_3$)$_2$, ^3J(H,H) = 6 Hz], 2.70 [sept, 5 H, C*H*(CH$_3$)$_2$, ^3J(H,H) = 6 Hz], 4.02 [s, 10 H, Cp(*C*H$_2$)$_5$], 6.91 (m, 20 H, C*H*$_{aryl}$). **^{13}C{^{1}H} NMR** (C$_6$D$_6$): δ = 24.29 [CH(*C*H$_3$)$_2$], 32.06 [*C*H(CH$_3$)$_2$], 34.12 [Cp(*C*H$_2$)$_5$], 124.78 (*C*), 124.97 (*C*), 125.10 (*C*), 126.45 (*C*), 127.62 (*C*), 127.94 (*C*), 128.53 (*C*), 128.84 (*C*), 129.16 (*C*), 139.32 (*C*), 146.10 (*C*). Elemental analysis failed due to different amounts of pentane within the crystals. Thus, we did not succeed to obtain a pentane free compound, although the crystals loose pentane, which is obvious from the fact that the transparent crystals become opaque when taken out of the mother solution.

X-ray Crystallography: The data were collected at 100 K with a Bruker APEX II diffractometer employing monochromated Mo-K_α radiation (λ = 0.71073 Å) from a sealed tube and equipped with an Oxford Cryosystems cryostat. The structure was solved by direct methods and refined by full-matrix least-square techniques (programs used: SHELXS and SHELXL).[23] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated using a riding model. In the case of polymorph **I** the refinement was performed with

Table 1. Crystal data and details of structural determination.

	GeCp$^{big}_2$·pentane (**I**)	GeCp$^{big}_2$·0.5pentane (**II**)
Formula wt.	1595.87	1560.80
T /K	100	100
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a /Å	14.4065(8)	17.7628(12)
b /Å	15.2167(8)	25.0590(17)
c /Å	24.8952(13)	21.2198(14)
α /°	85.095(2)	90
β /°	81.266(2)	99.890(2)
γ /°	64.182(2)	90
V /Å^3	4854.6(4)	9305.0(11)
Z	2	4
μ /mm^{-1}	0.362	0.377
δ /g·cm^{-3}	1.092	1.114
Radiation source /Å	0.71073	0.71073
Θ-range /°	1.49 to 24.22	1.42 to 27.59
Index-range	$-15 \le h \le 16$	$-22 \le h \le 23$
	$-17 \le k \le 16$	$-30 \le k \le 32$
	$-28 \le l \le 28$	$-27 \le l \le 27$
Reflections measured	64084	173312
Independent reflections	15022	21099
R(int.)	0.0512	0.0475
Goof	1.078	1.139
Parameters / restrains	1045 / 0	1044 / 25
Min / max e-density /e·Å^{-3}	–0.774 / 0.794	–0.611 / 1.036
Final *R* indices $I > 2\sigma$	R_1 = 0.0637	R_1 = 0.0641
	wR_2 = 0.1587	wR_2 = 0.1457
Final *R* indices (all data)	R_1 = 0.1025	R_1 = 0.0937
	wR_2 = 0.1742	wR_2 = 0.1604

Dedicated Cluster

solvent-free reflection data following PLATON/squeeze run. A refinement of the untreated reflection data set produces several peaks with 2.4–3.0 e•Å^{-3} corresponding to a highly disordered pentane molecule. The peaks attributed to carbon atoms result in R_1 = 0.066. The SQUEEZE refinement revealed a void with a volume of 207 Å^3 at the position 0.5, 0, 1.[24] Table 1 contains the crystal data and details of the X-ray structural determination for both polymorphs (**I** and **II**) of $GeCp^{big}_2$ (**1**).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-876429 (**I**) and CCDC-876430 (**II**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support.

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[16] The bond lengths as well as angles within **1** are only slightly different between both polymorphs; e.g. the Cp–Ge–Cp angle β is 160.9° in the case of polymorph **I**, whereas it is 161.6° in the case of the polymorph **II**.

[17] The calculated density of polymorph **I** is only 1.092 g•cm^{-3}, whereas it is 1.114 g•cm^{-3} for polymorph **II**. However in the case of polymorph **I** there are large voids (200 Å^3) present within the structure where another solvent molecule is localized, but which could not be refined during structure solution. The size of the void thus gives space for another pentane molecule, which would increase the calculated density to 1.116 being thus comparable to the density of polymorph **II**. Hence the density of both polymorphs is quite similar but polymorph **I** exhibits a larger amount of co-crystallizing solvent molecules leading to a less dense packing of **1**.

[18] Quantum-chemical calculations were carried out with the RI-DFT version of the Turbomole program package by employing Grimme B97-D-functional. The basis sets were of TZVPP quality. The electronic structure was analyzed with the Ahlrichs-Heinzmann population analysis based on occupation numbers. Turbomole: O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346–354; B97-D-functional: S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787–1799; RI-DFT: K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283–290; TZVPP: A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835; Ahlrichs-Heinzmann population analysis: E. R. Davidson, *J. Chem. Phys.* **1967**, *46*, 3320–3324; K. R. Roby, *Mol. Phys.* **1974**, *27*, 81–104; R. Heinzmann, R. Ahlrichs, *Theor. Chim. Acta* **1976**, *42*, 33–45; C. Erhardt, R. Ahlrichs, *Theor. Chim. Acta* **1985**, *68*, 231–245.

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Received: May 24, 2012
Published Online: August 14, 2012

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